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CO₂ Capture in Wet and Dry Superbase Ionic Liquids

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Abstract

The solubility of carbon dioxide (CO₂) in five tetraalkylphosphonium superbase ionic liquids, namely the trihexyltetradecylphosphonium phenoxide, trihexyltetradecylphosphonium benzotriazolidide, trihexyltetradecylphosphonium benzimidazolidide, trihexyltetradecylphosphonium 1,2,3-triazolidide and trihexyltetradecylphosphonium 1,2,4-triazolidide was studied experimentally under dry and wet conditions at 22 °C and at atmospheric pressure using a gravimetric saturation technique. The effects of anion structure and of the presence or absence of water in solution on the carbon dioxide solubility were then deduced from the data. ¹H and ¹³C-NMR spectroscopy and ab initio calculations were also conducted to probe the interactions in these solutions, as carbon dioxide and water can compete in the ionic liquid structure during the absorption process. Additionally, the viscosity of selected superbase ionic liquids was measured under dry and wet conditions in the presence or absence of CO₂ to evaluate their practical application in carbon dioxide capture processes. Finally, the recyclability of the trihexyltetradecylphosphonium 1,2,4-triazolidide under dry and wet conditions was determined to probe the ability of selected solvents to solubilize chemically a high concentration of carbon dioxide and then release it within a low energy demand process.

Keywords

Carbon dioxide; superbase ionic liquids; dry and wet conditions; NMR spectroscopy; ab initio calculations

1 Introduction

The development of an economically viable carbon dioxide (CO₂) capture process is becoming increasingly important as concerns over global greenhouse gas emissions continue to grow. Current CO₂ capture technology use aqueous solutions of amines, *e.g.* monoethanolamine (MEA), to chemically absorb CO₂. The use of this process at the industrial scale is driven by the low cost of solvents used and their high reactivity with the CO₂, leading to a theoretical absorption capacity close to a 2:1 ratio (nCO₂:nsolvent). However, these advantages are offset by several disadvantages, *e.g.* the high energy demand to regenerate solvents, driven by the large enthalpy of absorption of CO₂ (-85 kJ·mol⁻¹ at 40 °C) [1] and heat loss through water vaporization, as well as the corrosion damage caused to the pipeline by the utilization of an amine solution [2,3].

Recent research has shown that ionic liquids (ILs) are promising sorbents for CO₂ capture, possessing beneficial properties such as thermal stability, negligible vapor pressure and chemical tunability [4]. Since the initial discovery that some ILs can have a high carbon dioxide solubility [5], many studies have been carried out to improve and understand the CO₂ solubilization [6-8]. However, the CO₂ absorption capacity due to physical absorption in ILs is still too low for practical application in a CO₂ capture process. Bates *et al.* [9] incorporated amine moieties into the IL structure and these materials showed enhanced CO₂ capture by chemical absorption; however, as found with the aqueous amine solvent systems, these ILs are limited by a 1:2 molar ratio (nCO₂:nIL). Zhang *et al.* [10] showed that the incorporation of an amine on both the cation and anion produced ILs with CO₂ absorption approaching equimolar values. Further studies by Gurkan *et al.* [11] showed that equimolar CO₂ capture can be achieved when the amine functionality is incorporated on just the anion. These results showed that in these ionic liquids, the two-step reaction to form the carbamate was hindered and dissolution can be achieved after the reaction of one amine, thereby enabling equimolar CO₂ absorption. Unfortunately, upon complexation with CO₂ and the subsequent formation of dense hydrogen-bonded networks [12], these amino acid ILs underwent a large increase in viscosity making a practical application in CO₂ capture unlikely [10,13-15].

More recently ILs with superbasic/aprotic heterocyclic anions (AHAs) which showed reversible equimolar CO₂ capture have been studied. These ILs show only small increases in viscosity after CO₂ absorption (< 200 mPa·s at 22 °C) unlike the amine-based ILs previously discussed [16-21]. The ability to capture more than 1:1 mole ratio has been demonstrated in a

set of ILs where more than one CO₂ interacting site has been incorporated into the anion, with results showing the ability to achieve a ratio of up to 1.60 nCO₂:nIL [22].

Flue gases contain large percentages of water vapor and for ILs to be applicable in CO₂ separation processes, they therefore must have the ability to absorb CO₂ in the presence of water. The presence of water can affect the physical properties of the IL [23] and it also has the potential to compete with the CO₂ for absorption sites [15]. Previous reports have shown that water can have both a positive or a negative effect on CO₂ absorption, depending on the IL structure and the concentration of water. Brennecke *et al.* reported a reduction of viscosity with only a small decrease in CO₂ absorption when a set of amine functionalized anion-tethered ionic liquids were examined [15]. These results were also corroborated by studying the effect of water on amino acid anion-based ILs [24]. In both cases, this effect was attributed to the decrease in CO₂ absorption due to a reprotonation of the anion. Theoretical and experimental studies of the effect of water on dialkylimidazolium acetate-based ILs showed that water inhibits both the chemical reaction and physical solubility of CO₂ [25]. However, these effects were only observed at high water concentrations, whereas further studies showed that the addition of small amounts of water to these ILs could result in an increase in CO₂ uptake [26]. Wang *et al.* also reported an increase in CO₂ absorption when water was added to phenolate-based ILs and they attributed this increase to bicarbonate formation [20]. They also reported studies with water for pyridine-containing anion functionalized ILs which exhibited high CO₂ absorption due to multiple CO₂ binding sites. However, in this case the ILs exhibited a decrease in CO₂ uptake ratio (nCO₂:nIL) by 0.1 [22]. In contrast, no significant change in CO₂ uptake was observed when dry and wet samples of ILs based on 1,2,3-triazolide were tested [27]. Recently, Brennecke *et al.* reported the CO₂ uptake under wet conditions for [P₆₆₆₁₄][2-CNPyr]. Therein, an enhanced CO₂ absorption over the dry studies was observed and NMR studies revealed that, unlike the other amino acid ILs reported, this IL did not suffer from anion reprotonation [21].

In this paper, the effect of water on CO₂ absorption in a set of tetraalkylphosphonium superbase ILs is reported. ILs with a variety of anions were synthesized, where anions were selected to give ILs with a range of CO₂ absorption capacities. Trihexyltetradecylphosphonium 1,2,4-triazolide ([P₆₆₆₁₄][124Triz]), trihexyltetradecylphosphonium phenoxide ([P₆₆₆₁₄][PhO]) and trihexyltetradecylphosphonium benzotriazolide ([P₆₆₆₁₄][Bentriz]) were chosen to represent ILs with high, medium and low CO₂ uptake [16,19,20]. To further enhance this study, trihexyltetradecylphosphonium benzimidazolide ([P₆₆₆₁₄][Benzim]) and

trihexyltetradecylphosphonium 1,2,3-triazolide ([P₆₆₆₁₄][123Triz]) were also chosen to investigate the effect of structural changes within the IL on CO₂ absorption, *e.g.* the addition of a benzene ring and the position of the nitrogen atoms in the ring, especially under dry vs. wet conditions, as, recently, dry studies of [P₆₆₆₁₄][Benzim] and [P₆₆₆₁₄][123Triz] have been reported [21]. Additionally, the effect of water on CO₂ absorption was observed by comparing the CO₂ uptake under dry and wet conditions and these materials were then analyzed using NMR spectroscopy. Furthermore, the changes in viscosity of selected samples under dry and wet conditions in the presence or the absence of CO₂ were also analyzed to evaluate the practical application of selected superbase ILs in CO₂ capture processes. Finally, *ab initio* calculations were employed to identify and quantify the interactions of the CO₂ and water with the ionic liquid moieties.

2 Methods

2.1 Materials and Superbase ILs Synthesis

With the exception of [P₆₆₆₁₄]Cl, which was received from Cytec (97.7 %), all IL precursors were purchased from Sigma-Aldrich, 1,2,4-triazole (98 %), phenol (99+ %), benzotriazole (99 %), 1,2,3-triazole (97 %) and benzimidazole (98 %). Gaseous nitrogen (99.998 %) and carbon dioxide (99.99 %) were obtained from BOC and passed through drying columns before contact with the IL samples. The water was purified using a Milli-Q 18.3 M Ω water system.

The superbase ILs were prepared using a two step synthesis; [P₆₆₆₁₄][OH] was synthesized using an anion exchange resin from [P₆₆₆₁₄]Cl. A column was packed with 50 cm³ ion exchange resin (Amberlite IRN-78, OH-form, from Sigma Aldrich) and the resin was washed with absolute ethanol to wet it sufficiently and remove any air from the resin. 35 g of [P₆₆₆₁₄]Cl was mixed with 25 cm³ of ethanol and this solution was poured into the column and flowed through the resin slowly. The product containing ethanol and [P₆₆₆₁₄][OH] was passed through the column three times to completely exchange the chloride anion with hydroxide anion. The product was collected in a 250 cm³ single-neck round bottom flask and the flask was then sealed. The amount of [P₆₆₆₁₄][OH] in its ethanol solution was then determined by ¹H NMR. Using a 1:1 mol ratio, the necessary amount of superbase was added into the solution and stirred for at least 8 h at room temperature. The solution was then dried under rotary evaporation and high-vacuum (50 °C) to obtain dry pure ILs.

2.2 Analysis

The structure and purity of the ionic liquids were analyzed using ^1H -NMR, ^{13}C -NMR and ^{31}P -NMR using a Bruker Avance 400 MHz Ultra shield Plus. The IL NMRs were carried out neat in the presence of a glass capillary insert containing deuterated solvent ($\text{DMSO-}d_6$). Gas tight NMR experiments were carried out using a valved NMR tube for intermediate pressure (up to 7 bar) supplied by Norell. The water content of the ILs were measured using a Metrohm 787 KF Titrino Karl Fischer and contained $< 0.1 \text{ wt\%}$ for all dry ILs.

The densities of the pure IL samples at 0.1 MPa were measured using a Mettler Toledo DM40 density meter at $25 \text{ }^\circ\text{C}$ with an accuracy of $\pm 0.01 \text{ }^\circ\text{C}$ by means of built-in precise Peltier thermostat. As recommended by the constructor, the densitometer was calibrated prior to measurements with degassed water and dehumidified air at atmospheric pressure. The uncertainty of the density is close to $1 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}$.

The decomposition temperatures of the pure IL samples were measured using a Mettler Toledo Star-e thermogravimetric analyser (TGA). This was carried out between 25 to $700 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under N_2 and decomposition temperatures are stated as the temperature at which 10 % weight loss is observed. Reported thermal properties are given with accuracy close to $\pm 1 \text{ }^\circ\text{C}$.

The viscosity of the IL samples was measured before and after CO_2 absorption using a Bohlin Gemini Rotonetic Drive 2. The temperature in the cell was regulated at $(25 \pm 0.01) \text{ }^\circ\text{C}$ controlled by a built-in precise Peltier thermostat. The viscosity standard (ASTM Oil Standard S600 of CANNON, $1053 \text{ mPa}\cdot\text{s}$ at $25 \text{ }^\circ\text{C}$) and ultra-pure water were used to calibrate the viscometer. Based on which, the uncertainty of reported viscosity measurements is close to $\pm 1 \text{ \%}$.

2.3 CO_2 Absorption and Desorption Experiments

All the ILs were stored and weighed out into a small vial with a septum lid (1.9 cm^3) in an argon-filled glove box within an uncertainty close to $1 \times 10^{-4} \text{ g}$. Additionally, all CO_2 uptake measurements in this study are recorded as the molar ratio of CO_2 and the IL, $n\text{CO}_2:n\text{IL}$.

2.3.1 Dry CO_2 absorption measurements

The IL ($\sim 0.5 \text{ g}$) was pre-treated by bubbling with nitrogen at $80 \text{ }^\circ\text{C}$ for 1 h at a flow rate of $50 \text{ cm}^3\cdot\text{min}^{-1}$ to dry the sample and the weight of the sample was recorded on an electronic

balance with an accuracy of ± 0.1 mg. This procedure was tested as a function of time and no weight change was observed for longer pre-treatments. The sample was then bubbled with dry CO₂ at a flow rate of 50 cm³·min⁻¹ at room temperature (22 ± 0.1 °C) for the required period of time and the weight gain used to calculate the amount of CO₂ absorbed (taking into account the mass of the headspace). The CO₂ absorption was monitored at intervals 5, 15, 30, 60 min and then left overnight (16 h).

2.3.2 Wet CO₂ absorption measurements

The IL (~ 0.5 g) was bubbled with N₂ containing 3 vol% H₂O at a flow rate of 50 cm³·min⁻¹ at room temperature (22 ± 0.1 °C) until the IL was saturated (*i.e.* until a stable weight was observed). The wet N₂ was generated by passing N₂ at a flow rate of 50 cm³·min⁻¹ through a water saturator held at 22 °C. Wet CO₂ containing 3 vol% H₂O was generated by passing CO₂ at a flow rate of 50 cm³·min⁻¹ through the same water saturator at 22 °C and flowed through the IL sample at room temperature (22 ± 0.1 °C). The weight change was recorded and used to calculate the amount of CO₂ absorbed (taking into account the mass of the headspace). During the wet CO₂ absorption studies the ILs were monitored at 5, 15, 30, 60 min and every hour until two consecutive weights was observed. Saturating the IL before CO₂ absorption and using wet CO₂ during the absorption should limit the change in water content throughout the absorption process. However, a Karl Fischer analysis of each IL sample after saturation of water under N₂ and after addition of CO₂ under wet conditions was carried out to monitor any changes in the water content during wet CO₂ absorption experiments.

2.3.3 CO₂ absorption/desorption measurements

CO₂ absorption/desorption experiments were carried out by bubbling with (dry or wet) CO₂, generated as described above, for 2 h then the CO₂ was desorbed by heating the IL to 80 °C under a flow of N₂ at 50 cm³·min⁻¹ for 15 min. After each cycle the weight returned to the original sample weight before adsorption ± 1 %.

2.4 Computational

Geometry optimisations and energy calculations were performed according to the Density Functional Theory (DFT) level of theory. The Gaussian 09 Rev C suite of programs was used for all the calculations [28], employing the Minnesota functional M06 [29] with a Pople basis set 6-311+G(d,p) [30]. For all the geometries optimized, the nature of the steady states

(minimum and transition state) were verified by analytical frequency calculations. The 3D representations have been drawn with CYLview [31].

3 Results and Discussion

3.1 CO₂ Solubility in Superbase ILs

The CO₂ solubility in the five synthesized ILs (Figure 1) was determined gravimetrically under dry and wet conditions at room temperature (22.0 ± 0.5 °C) and at atmospheric pressure. The dry results for each of the tested ILs are consistent with previously reported results in the literature [19,21]. For example, we obtained CO₂ absorption capacities for [P₆₆₆₁₄][124Triz], [P₆₆₆₁₄][PhO] and [P₆₆₆₁₄][Bentriz] of 0.92, 0.49 and 0.23, respectively. For comparison, Wang *et al.* [19] reported values close to 0.95, 0.50 and 0.17 for the same ILs under the same conditions. Such comparison demonstrates the accuracy of the experimental method and set-up used in this work.

Figure 1 and Table S1 of the supporting information show a comparison of dry and wet CO₂ absorption data over time for all five ILs tested. Equimolar CO₂:IL absorption was achieved using the [P₆₆₆₁₄][124Triz] or [P₆₆₆₁₄][Benzim] ILs after 1 h and only a small increase in CO₂ absorption was further observed when each system was equilibrated during 16 h. However, the other selected ILs showed a lower CO₂ uptake under dry conditions; for example, [P₆₆₆₁₄][PhO] has an absorption of 0.5 after 1 h which increases to an equimolar ratio after 16 h. However, in comparison with other tested ILs, both [P₆₆₆₁₄][123Triz] and [P₆₆₆₁₄][Bentriz] showed low CO₂ absorption molar ratios after 1 h, close to 0.35 and 0.23, which increased to 0.62 and 0.39 after 16 h, respectively.

As expected, the addition of water to the system led to an enhancement in the rate of CO₂ absorption in the solution owing to the decrease in viscosity of the wet IL samples compared with the dry systems. For example, in the case of the [P₆₆₆₁₄][124Triz], [P₆₆₆₁₄][123Triz] and [P₆₆₆₁₄][Bentriz] solutions, the maximum CO₂ absorption can be reached within 30 min of exposure to CO₂ [21].

During the wet tests the water content was analyzed before and after CO₂ absorption to probe changes in the water level in solution. To accurately compare the dry and wet results, the change in water content was taken into account and the absorption results adjusted accordingly (Table 1). From the results, variations in the effect of the water on CO₂ capture capability are observed depending on the anion of the IL. For the [P₆₆₆₁₄][124Triz] and

[P₆₆₆₁₄][Benzim] ILs a reduction in the CO₂ absorption capacity is observed under wet conditions from 0.99 to 0.88 and 1.20 to 0.89, respectively. In the case of [P₆₆₆₁₄][PhO], initially, the addition of water led to an increase in the sample mass following the CO₂ absorption over the first 30 min compared with the dried sample. However, after 30 min a sharp decrease in the weight recorded was observed which then stabilized after 6 h at a much lower value (0.16) than found for the dry test (Figure 1b). Figure 2 shows how the IL changes visibly as a function of time on addition of CO₂. Initially, the IL becomes cloudy and resembles an emulsion. After 60 min, the emulsion cleared and the solution became clear, which corresponds to the time when the sample weight decreased again. The creation of the emulsion could be due to the change in the chemical structure of the IL as the CO₂ comes into contact with the water molecules and the [P₆₆₆₁₄][PhO]. As the CO₂ is added to the sample it competes with the water for binding with the anion leading to the formation of the emulsion. The reason that this may be observed in the [P₆₆₆₁₄][PhO] but not in the other ILs tested could be due to an increase of hydrogen-bonding with oxygen in the phenoxide compared with the nitrogen-containing anions. As the sample continues to be treated with CO₂, the water within the emulsion is evaporated and some condensation on the side of the vial appears before the emulsion and the condensation is eventually removed. The initial weight gain is, therefore, due to the interaction of the CO₂ with the IL system before the weight decreases again due to evaporation of the water and the system reaching equilibrium. Unlike the other ILs, the Karl Fischer analysis of the wet [PhO]⁻ based IL did not match the value calculated from the weight gain during treatment with wet N₂. The result was compromised by the reprotonation of the phenoxide and the subsequent reaction of phenol with the Karl Fischer reagents. Therefore, without an accurate initial Karl Fischer value, an adjusted CO₂ absorption value could not be calculated. However, studies of the [P₆₆₆₁₄][PhO] showed that this IL is unstable and that after reaction with CO₂ the IL becomes more viscous and turns black, whereas it is not possible to regenerate the IL indicating some irreversible reaction/decomposition. In other words, the low absorption capacity under wet conditions and instability of [P₆₆₆₁₄][PhO] makes it an unlikely candidate for an efficient CO₂ separation technique.

In contrast, in the case of the [P₆₆₆₁₄][123Triz] and [P₆₆₆₁₄][Bentriz] ILs, the addition of water has a positive effect on their CO₂ absorption, showing increases from 0.35 to 0.86 and 0.26 to 0.63, respectively. It is important to note that the CO₂ uptake in these ILs under wet conditions is not just faster than under the dry conditions, but that the CO₂ absorption after 1 h wet is higher than the maximum absorption under dry condition after 16 h. Under dry

conditions the CO₂ capture capability of these ILs after 1 h seems to increase according to the following order: [P₆₆₆₁₄][Bentriz] < [P₆₆₆₁₄][123Triz] < [P₆₆₆₁₄][PhO] < [P₆₆₆₁₄][124Triz] < [P₆₆₆₁₄][Benzim]; the same trend is observed after 16 h with the lowest value being 0.39. The trend is slightly modified after the addition of water: [P₆₆₆₁₄][Bentriz] < [P₆₆₆₁₄][123Triz] < [P₆₆₆₁₄][124Triz] ~ [P₆₆₆₁₄][Benzim] with all values being greater than 0.6. The best IL under dry conditions is [P₆₆₆₁₄][Benzim], whereas under wet conditions [P₆₆₆₁₄][Benzim] and [P₆₆₆₁₄][124Triz] both exhibit the greatest CO₂ capacity.

From a practical point of view, the ability of selected solvents to capture a high concentration of CO₂ and then release the CO₂ within a low energy demand during the regeneration process is essential. This ability has been demonstrated previously for the [P₆₆₆₁₄][124Triz] under dry conditions, as Wang *et al.*[19] carried out 25 cycles and showed that its CO₂ capture is reversible without detrimental effects on CO₂ absorption capacity or rate. During this work, we have also investigated the recyclability of the [P₆₆₆₁₄][124Triz] under dry conditions, showing that after 5 cycles equimolar CO₂ absorption is still achieved. Additionally, 6 successive cycles of CO₂ absorption and desorption under wet conditions have been carried out (Figure 3) using the [P₆₆₆₁₄][124Triz] to show the recyclability of its CO₂ capture under wet conditions. Interestingly, after 6 cycles more than 97 % of the [P₆₆₆₁₄][124Triz] CO₂ uptake capacity is retained, showing that its CO₂ absorption is recyclable also under wet conditions. In other words, in the case of the [P₆₆₆₁₄][124Triz], the addition of water does not have any irreversible effects on the CO₂ uptake.

3.2 Viscosity

The viscosity of the ILs was monitored before and after CO₂ solubility tests in both dry and wet conditions and data are summarized in Table 2. As reported previously, in the dry systems, unlike the amino acid systems, only small increases in viscosity are observed upon the addition of CO₂ for this class of ILs [19]. In all the ILs investigated herein, the addition of water to the system results in a decrease in the viscosity from the dry measurements. For example, addition of water to [P₆₆₆₁₄][124Triz] reduced the viscosity of the medium from 569 to 114 mPa·s. Previous investigations of the effect of water on ILs showed this reduction in viscosity comes as a result of the water reducing the electrostatic attractions of the ions and causing a decrease in the overall cohesive energy of the system [23]. Table 2 also shows an increase in viscosity after the absorption of CO₂ by the wet IL. However, it should be noted that lower viscosity values were determined for the wet ILs after CO₂ absorption in

comparison to the corresponding dry IL after CO₂ exposure. For example, in the case of [P₆₆₆₁₄][124Triz], after CO₂ uptake the viscosity values under dry and wet conditions are 638 and 200 mPa·s, respectively. This general reduction in viscosity under wet conditions is likely to be the reason why the CO₂ uptake is faster in the wet ILs compared to the dry ILs. In contrast, wet studies of [P₆₆₆₁₄][2-CNPy] by Seo *et al.* [21] showed a dramatic increase in viscosity after the absorption of CO₂ resulting in a viscosity larger than the neat IL. The different trend in viscosity observed could be attributed to the larger amounts of water used in the present study.

3.3 NMR and Computational Studies

NMR studies have been carried out to investigate the changes in the interactions which occur on the addition of water and CO₂ absorption. As also shown in previous studies [19], ¹³C-NMR spectra of the CO₂-saturated ILs show the appearance of a peak at ~ 160 ppm in all samples, attributed to the formation of the carbamate species. It should be noted that the carbamate peak could only be observed in the dry [P₆₆₆₁₄][Bentriz] + CO₂ ¹³C-NMR spectra, using a gas tight NMR tube, which suggests that the small amount of CO₂ absorbed is weakly bound to the IL. Table 3 reports the ¹³C-NMR shifts for the carbamate peak observed in each IL under dry and wet conditions, showing that similar peak positions are found irrespective of the presence or absence of water. ¹³C-NMR spectra obtained for [P₆₆₆₁₄][Bentriz] IL after CO₂ absorption under dry and wet conditions are shown in Figure 3. Integration of the carbamate peak (normalized to the IL peaks) shows a mole ratio of 0.21 and 0.57 in the dry and wet IL, respectively, which correspond well to the results obtained using the gravimetric analysis (Table 1) and confirms the enhanced CO₂ absorption in [P₆₆₆₁₄][Bentriz] IL under wet conditions. No other notable changes were observed in the ¹³C-NMR spectra, as reported in Figures S1-S4 of the supporting information. ³¹P-NMR was also carried on the CO₂ saturated ILs under both dry and wet conditions. In each case, only one main peak was observed at ~34 ppm and no changes in the peak were observed before and after CO₂ absorption under both dry and wet conditions, confirming that no chemical change is occurring in the cation environment.

Figures 5 to 8 show a comparison of the ¹H-NMR spectra obtained for each of the ILs under dry and wet conditions, before and after CO₂ absorption. In all cases, the protons associated with the anion show the same trends under dry and wet conditions. A small shift downfield is observed after absorption of CO₂ in the dry IL, which is associated with the formation of the

carbamate species. On addition of water to the pure IL a downfield shift is also found associated with protonation of the IL. After CO₂ absorption in the wet IL, a further shift downfield is observed, compared with the dry pure IL, due to the formation of the carbamate. Changes in the protons attached to the cation are also observed; in particular, the peak which occurs between 1.5-2.0 ppm, corresponding to the P⁺-CH₂- protons, shifts significantly under the conditions studied. In all cases the addition of water to the IL before CO₂ absorption shows a shift in this peak of 0.35-0.15 ppm upfield of the dry IL (Figures 5-8 (a) and (c)). This shift is associated with the reprotonation of the anion and the subsequent interaction of the OH⁻ formed with the cation [27]. These changes observed in the ¹H-NMR for the alkyl group attached to the phosphorous suggest that there is close interaction of the cation and anion in these ILs. Addition of CO₂ under dry conditions in all ILs studied results in a shift downfield of the peak corresponding to P⁺-CH₂- protons.

Simulations of the CO₂ interaction with the anion and the subsequent anion-cation geometry for the analogous [P₃₃₃₃]⁺-based systems showed an increase in the distance of the anion from the P⁺-CH₂- protons indicating a decrease in the interaction of the cation and anion. Figure 9 shows the calculated distances between the nitrogen atoms of the anion and the hydrogen atoms of the P⁺-CH₂- group for [P₃₃₃₃][124Triz] and [P₃₃₃₃][Bentriz] before and after addition of CO₂. The shortest distance increases from 3.03 to 3.36 Å and 2.81 to 3.21 Å for the [P₃₃₃₃][124Triz] and [P₃₃₃₃][Bentriz] ILs, respectively. In addition, the average distance increases from 3.11 to 3.70 and 3.11 to 3.52, respectively. This decreased interaction is due to the lower overall effective charge on the anion due to the formation of the carbamate. In general, the results show that the OH⁻ only has a small effect on the CO₂ uptake; after addition of CO₂ to the wet IL, shifts similar to the dry IL after CO₂ are observed. This shows that the CO₂ competes effectively with the H₂O for reprotonation; for example [P₆₆₆₁₄][124Triz] IL shows shifts of 1.98 and 1.80 ppm for dry IL after CO₂ and wet IL after CO₂, respectively. This finding is in agreement with the recorded CO₂ uptake values, which show a small decrease in CO₂ uptake with the addition of water to the system from 0.99 to 0.88. A comparison of the dry samples after CO₂ and the wet samples after CO₂ exhibits no correlation in shifts between the ILs that have improved or decreased CO₂ uptake under wet conditions, indicating that it is a fine balance between the interaction with the OH⁻ anion and carbamate. For example, similar chemical shifts for dry IL after CO₂ and wet IL after CO₂ in [P₆₆₆₁₄][124Triz] (1.98 and 1.80 ppm, respectively) and [P₆₆₆₁₄][123Triz] (1.90 and 1.80 ppm, respectively) are observed, regardless of the varying effect of water on CO₂ uptake.

4 Conclusions

In this work, five trihexyltetradecylphosphonium-based ionic liquids paired with superbase anions, namely the phenoxide, 1,2,3-triazolide, 1,2,4-triazolide, benzotriazolide, or benzimidazolide were synthesized to evaluate their CO₂ capture capability under dry and wet conditions at 22 °C and atmospheric pressure. Results obtained under dry conditions were compared with the literature to validate the experimental device and procedure used in this study. Additionally, the CO₂ solubility data under dry and wet conditions were compared to highlight the impact of anion structure and water content to screen the ionic liquids for detailed further study. This study, showed that from the selected anion structures, [Benzim]⁻ and [Bentriz]⁻ provide the highest and lowest CO₂ uptake, respectively. Depending on the anion structure, different effects of the water were also observed. For example, in the case of ionic liquids presenting equimolar CO₂ uptake under dry condition, *e.g.* [P₆₆₆₁₄][Benzim] or [P₆₆₆₁₄][124Triz], only small reductions were observed in their CO₂ uptake under wet conditions from >1 to 0.89 or 0.88, respectively. In contrast, a positive effect of the presence of water on CO₂ uptake was observed in the case of [P₆₆₆₁₄][Bentriz] and [P₆₆₆₁₄][123Triz]. However, due to its instability under wet conditions, [P₆₆₆₁₄][PhO] does not appear to be a good candidate for CO₂ separation techniques. The effects of the presence or the absence of water on CO₂ and ILs interactions were next evaluated using ¹H and ¹³C NMR spectroscopy and ab initio calculations. These results show that, generally, the CO₂ competes very well with H₂O for absorption. Additionally, a reduction in the ILs viscosity is observed in the wet systems even after addition of CO₂ to the IL (< 300 mPa·s) which makes these ILs more promising for practical application. Finally, the ability to repeatedly capture and release the CO₂ under wet conditions was also demonstrated, using [P₆₆₆₁₄][124Triz] as a probe, without significant reduction in its CO₂ capacity after 6 cycles.

5 Acknowledgements

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Figures and Tables

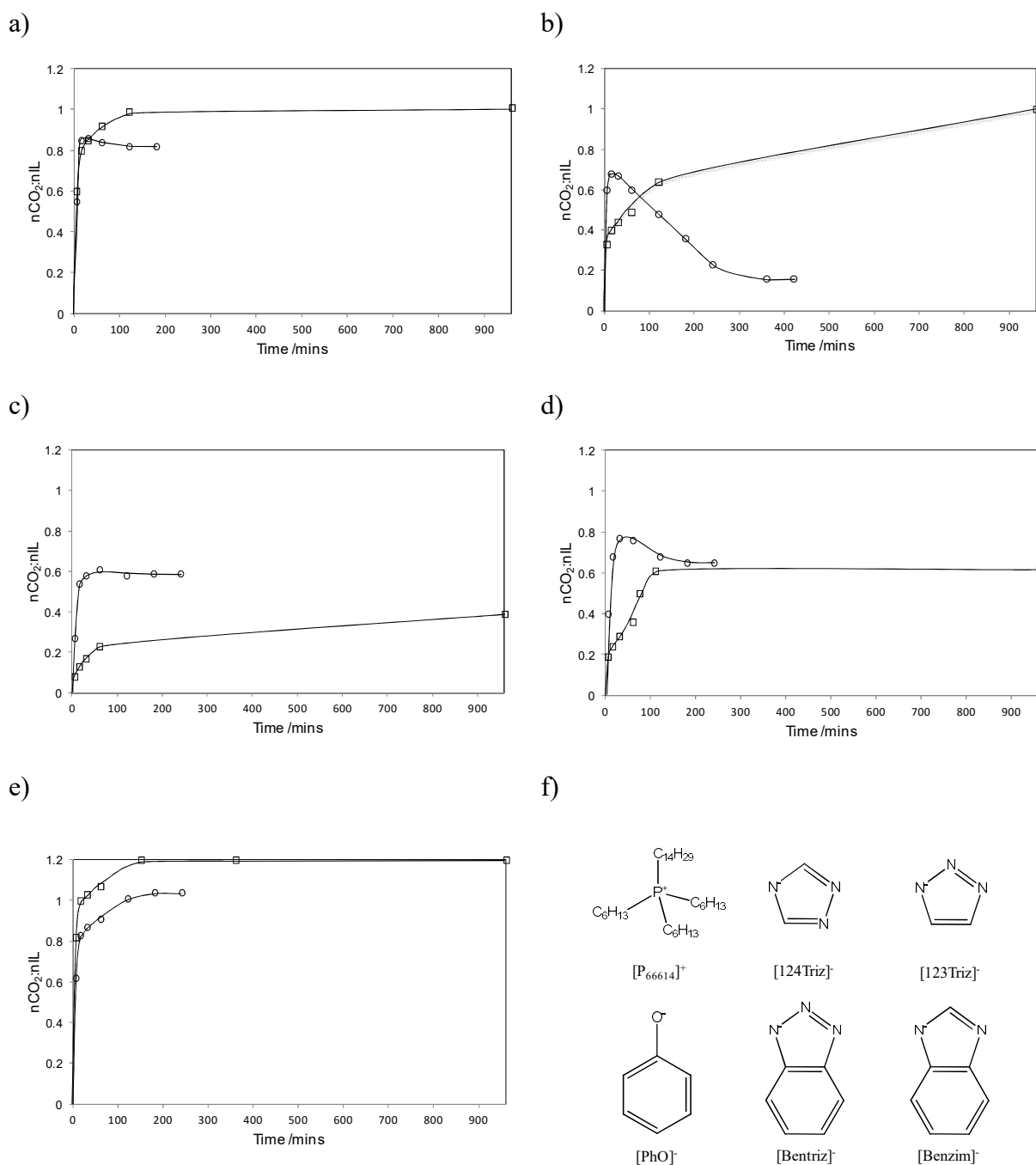


Fig. 1 CO₂ uptake over time under: \square , dry; and \circ , wet conditions for (a) [P₆₆₆₁₄][124Triz], (b) [P₆₆₆₁₄][PhO], (c) [P₆₆₆₁₄][Bentriz], (d) [P₆₆₆₁₄][123Triz] and (e) [P₆₆₆₁₄][Benzim]; (f) structures of the cation and anion in phosphonium superbase ILs studied. Solid lines are a guide to the eye.

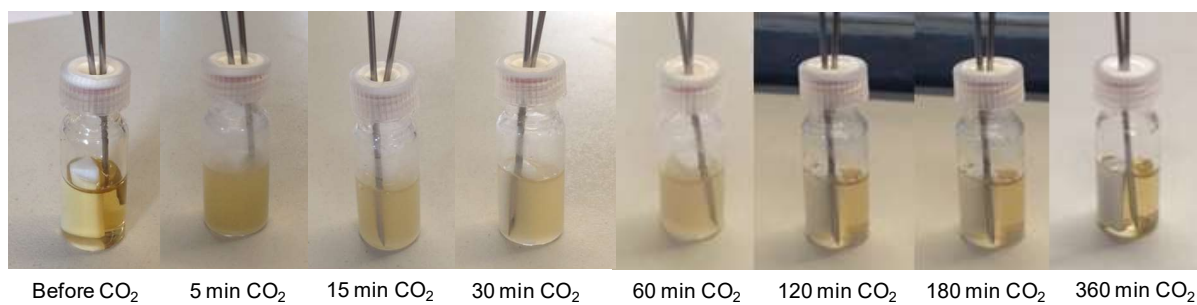


Fig. 2 Visible changes observed in the [P₆₆₆₁₄][PhO] IL as a function of the uptake of CO₂ under wet conditions.

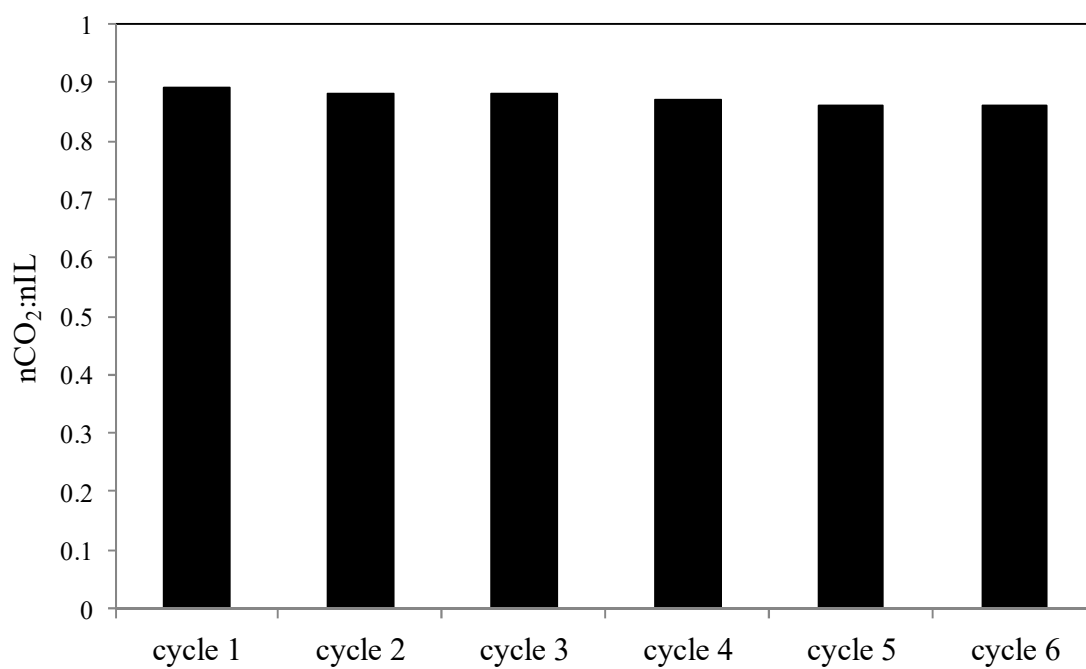


Fig. 3 Six absorption/desorption cycles using $[P_{66614}][124\text{Triz}]$ under wet conditions, CO_2 absorption was carried out for 2 h and desorption was performed under N_2 at 80 °C for 15 min.

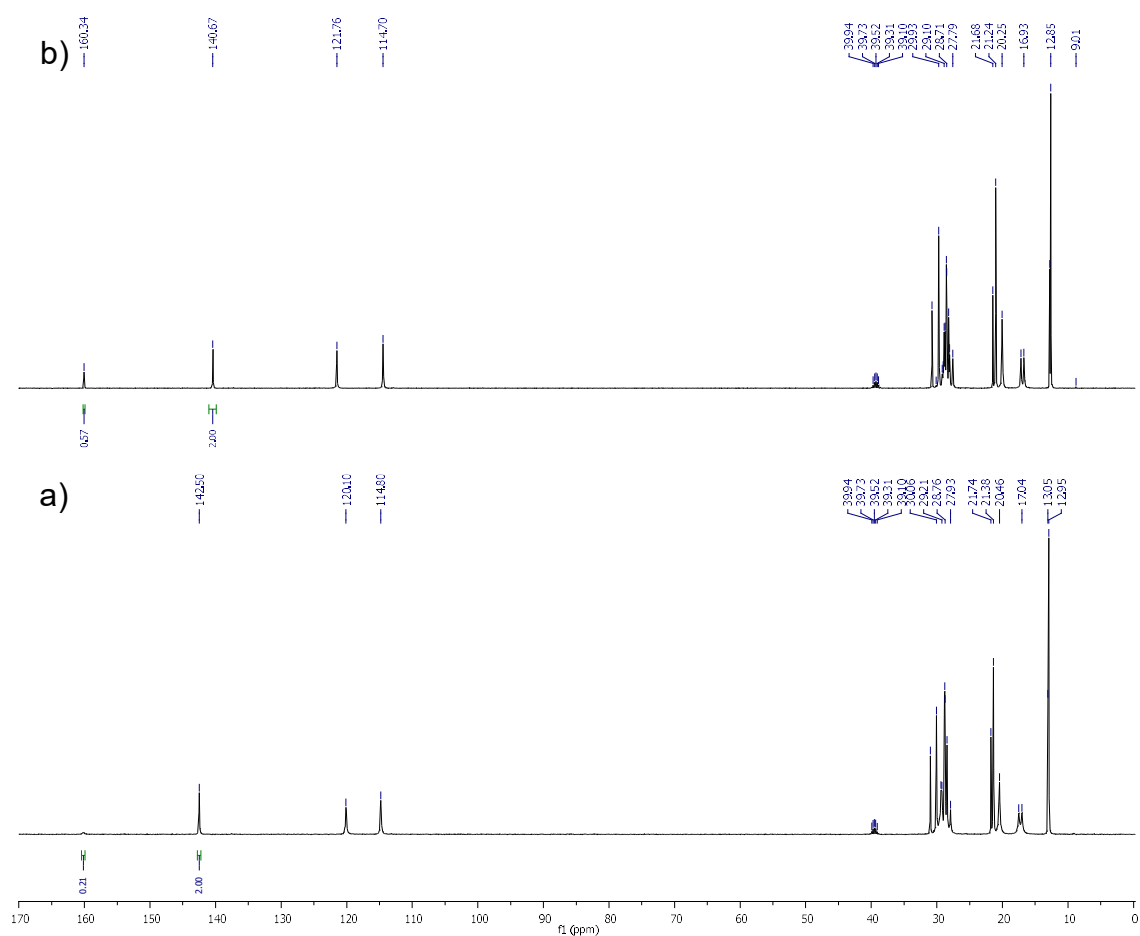


Fig. 4 ^{13}C -NMR of $[\text{P}_{66614}][\text{Bentriz}]$ after CO_2 absorption under (a) dry conditions and (b) wet conditions. Integrations shown to illustrate the consistency between the uptake values determined by both the NMR and the gravimetric methods.

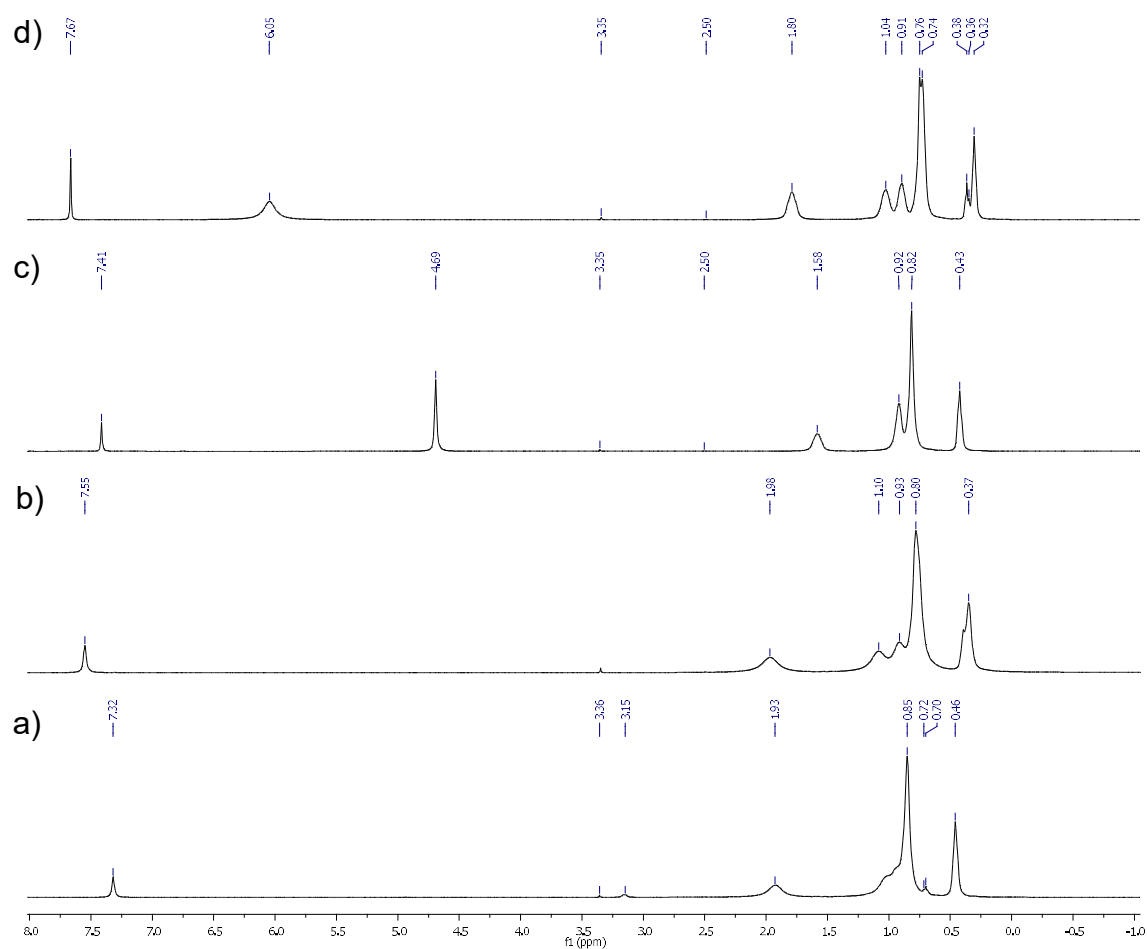


Fig. 5 ^1H -NMR of $[\text{P}_{66614}][124\text{Triz}]$ under (a) dry conditions, (b) dry conditions after CO_2 absorption, (c) wet conditions and (d) wet conditions after CO_2 absorption.

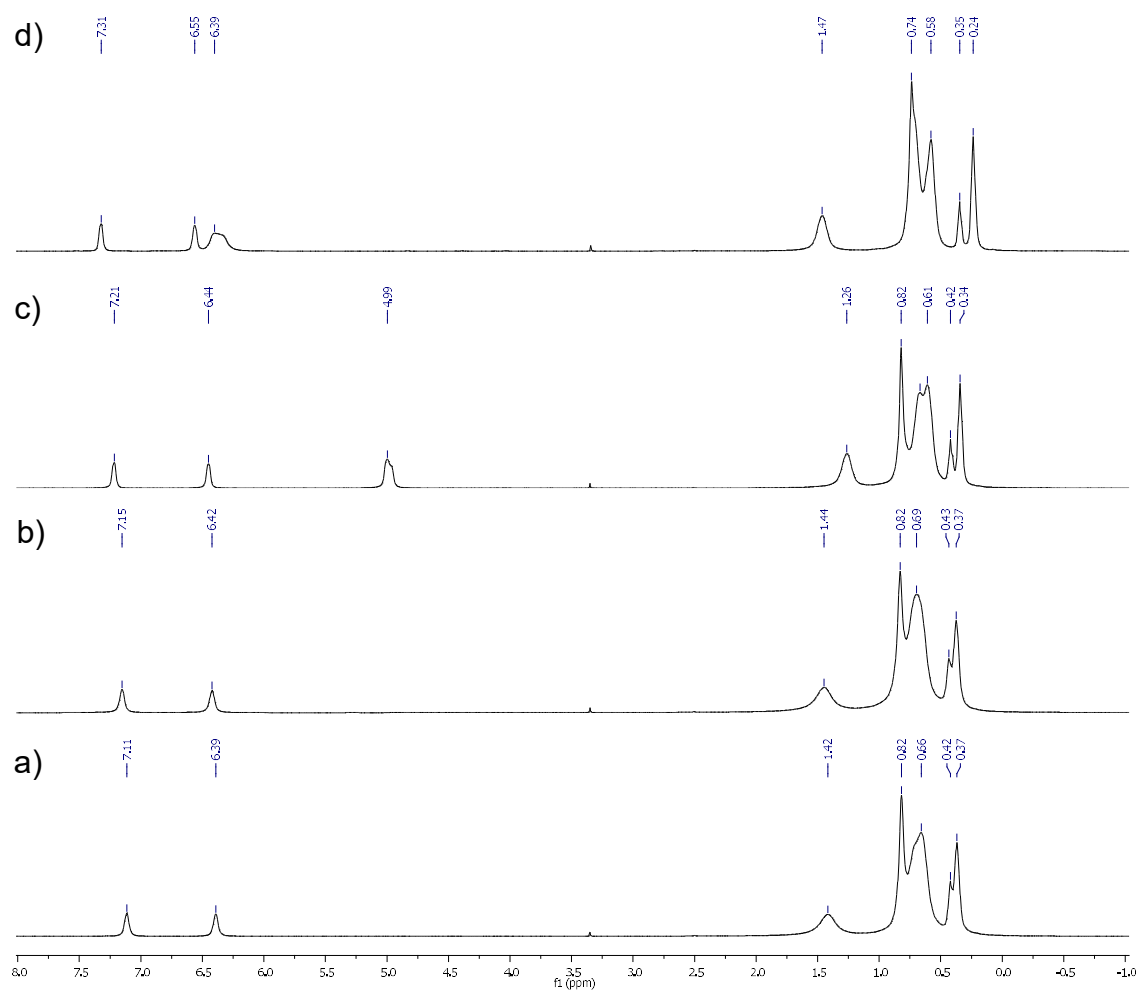


Fig. 6 ^1H -NMR of $[\text{P}_{66614}][\text{Bentriz}]$ under (a) dry conditions, (b) dry conditions after CO_2 absorption, (c) wet conditions and (d) wet conditions after CO_2 absorption.

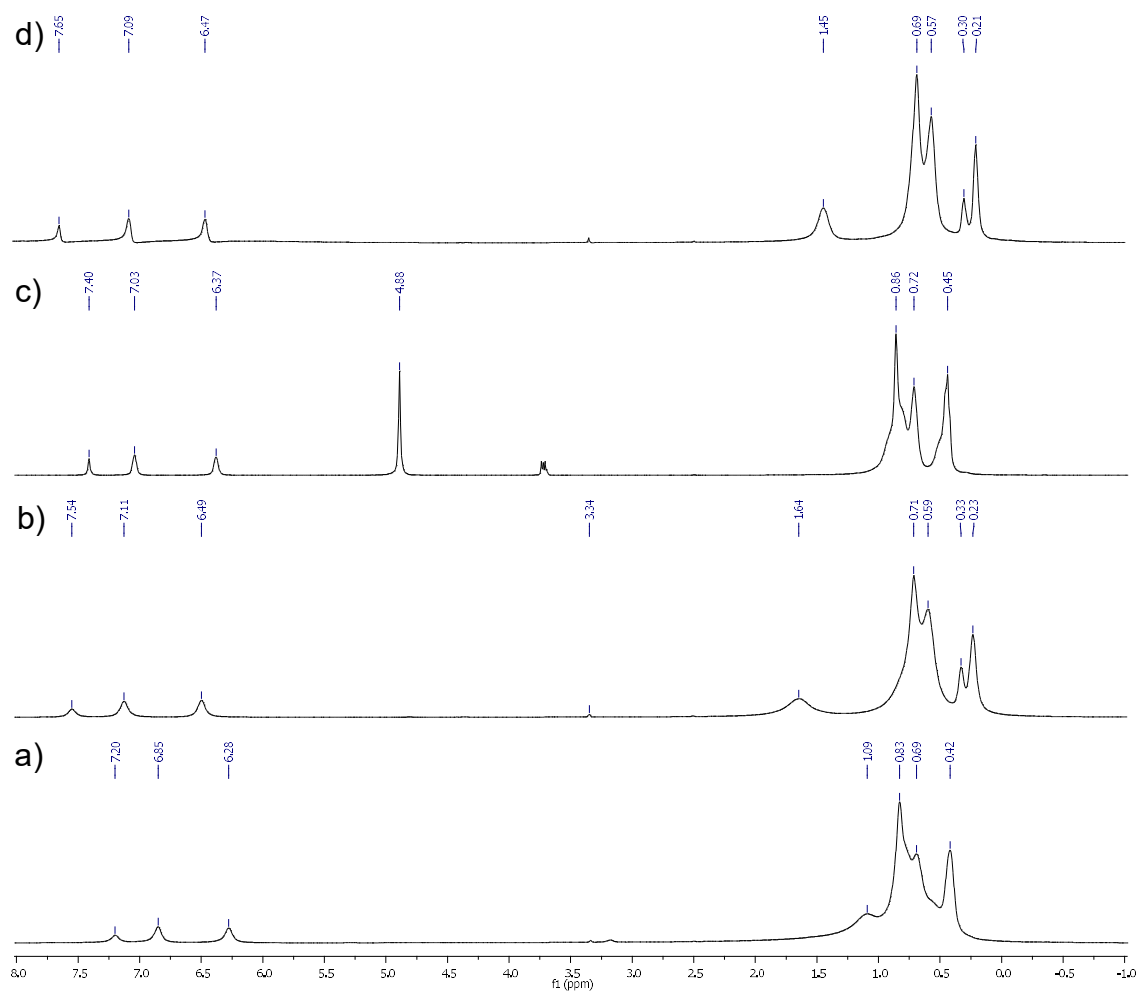


Fig. 7 ^1H -NMR of $[\text{P}_{66614}][\text{Benzim}]$ under (a) dry conditions, (b) dry conditions after CO_2 absorption, (c) wet conditions and (d) wet conditions after CO_2 absorption.

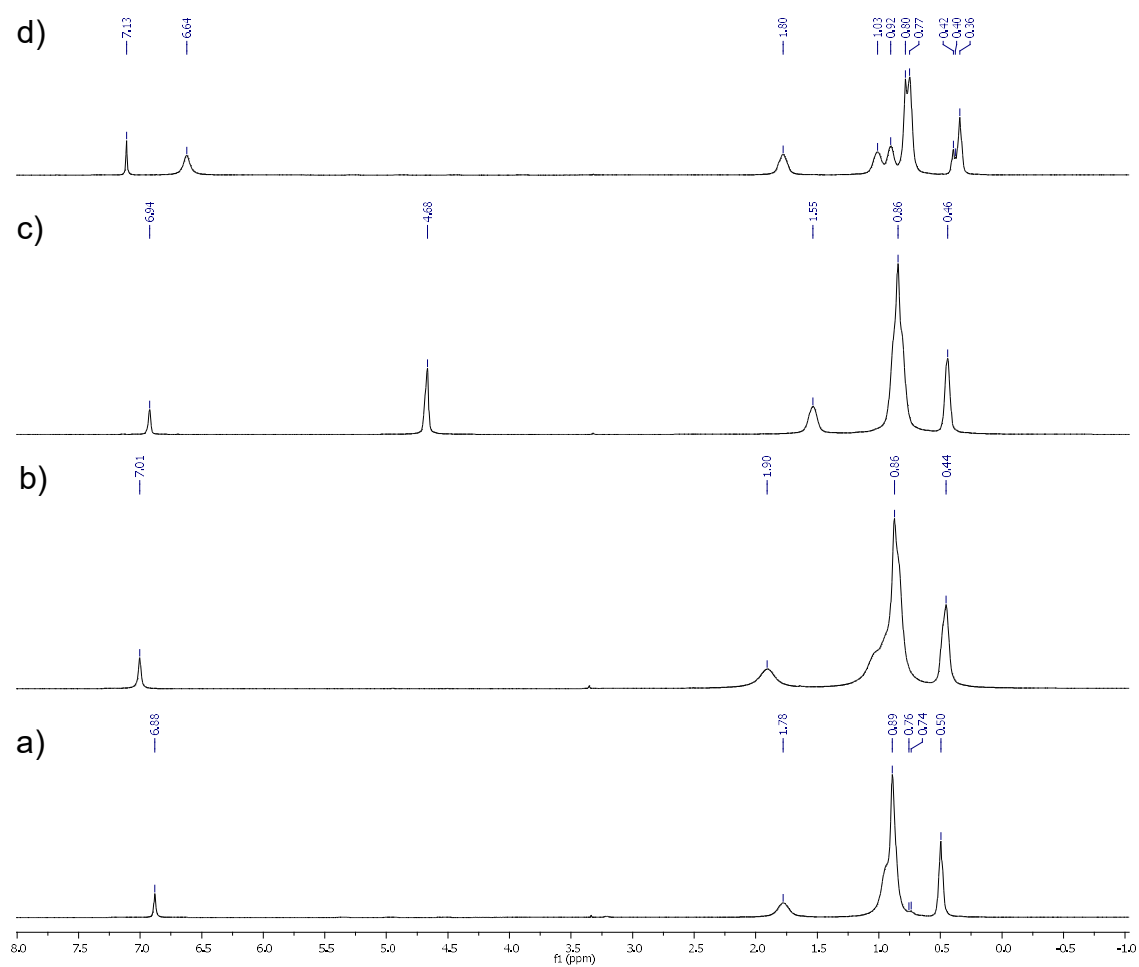


Fig. 8 ^1H -NMR of $[\text{P}_{66614}][123\text{Triz}]$ under (a) dry conditions, (b) dry conditions after CO_2 absorption, (c) wet conditions and (d) wet conditions after CO_2 absorption.

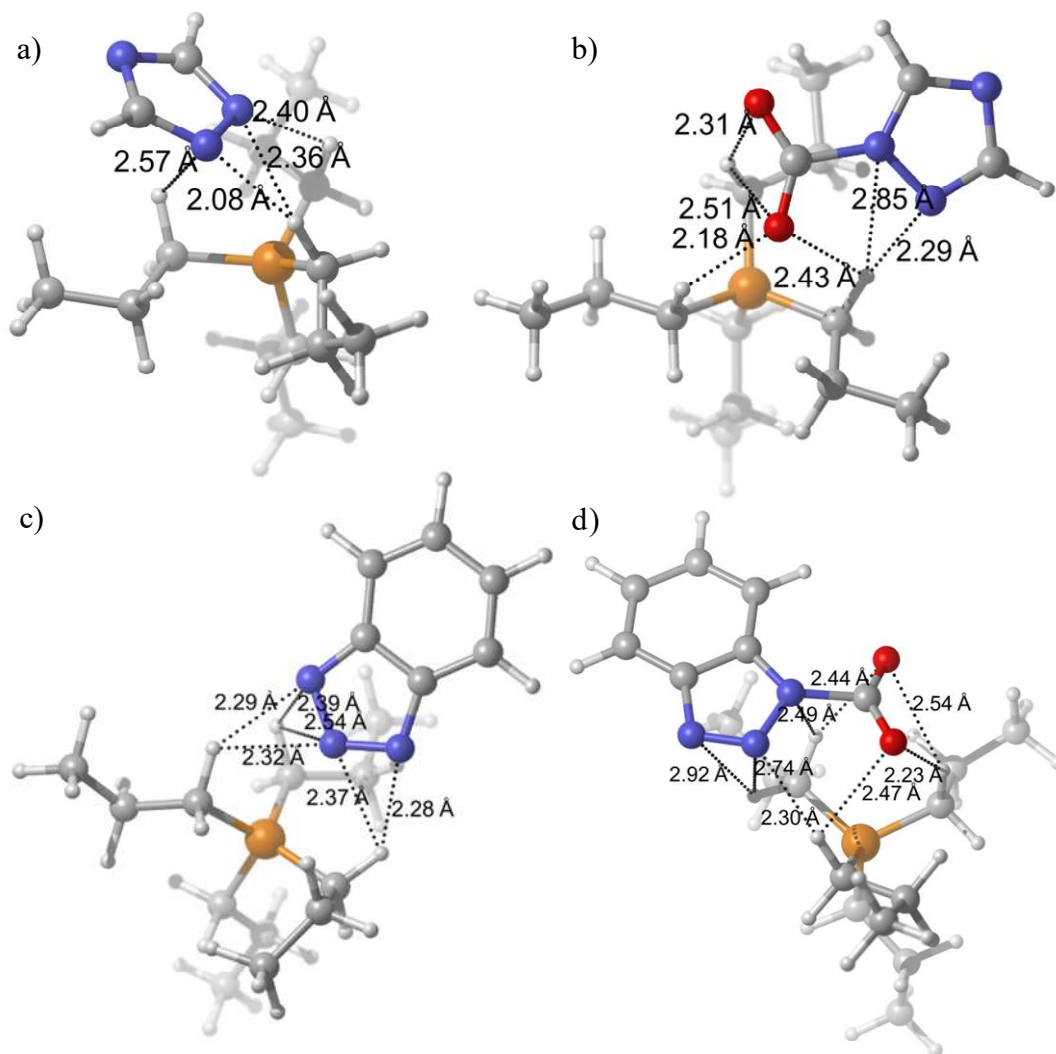


Fig. 9 Calculated structures showing the distances calculated between the nitrogen atoms of the anion and the hydrogen atoms: P-CH₂- of the cation as well as the oxygen atoms of the CO₂ and the hydrogen atoms: P-CH₂- of the cation for (a) [P₃₃₃₃][124Triz], (b) [P₃₃₃₃][124Triz] after CO₂ interaction, (c) [P₃₃₃₃][Bentriz] and (d) [P₃₃₃₃][Bentriz] after CO₂ interaction.

Table 1 Water content in ILs before and after CO₂ absorption measurements and CO₂ uptake adjusted for water content at 22 °C and atmospheric pressure.

| IL | Water content (wt %) | | | | CO ₂ uptake (nCO ₂ :nIL) | |
|--------------------------------|----------------------|-------------|-----------------------|------|--|----------------------------|
| | Wet | | Wet + CO ₂ | | | |
| | KF | Weight gain | KF | Dry | Wet | |
| | | | | | Calculated from mass change | Adjusted for water content |
| [P ₆₆₆₁₄][124Triz] | 11.27 | 10.37 | 10.78 | 0.99 | 0.82 | 0.88 |
| [P ₆₆₆₁₄][PhO] | 10.58 | 6.51 | 6.09 | 1.00 | 0.16 | - |
| [P ₆₆₆₁₄][Bentriz] | 7.42 | 6.56 | 7.17 | 0.23 | 0.59 | 0.63 |
| [P ₆₆₆₁₄][123Triz] | 11.57 | 10.22 | 9.83 | 0.61 | 0.65 | 0.86 |
| [P ₆₆₆₁₄][Benzim] | 8.62 | 8.10 | 9.76 | 1.20 | 1.04 | 0.89 |

$u(\text{water content}) = (0.01 \times \text{water content}) \text{ wt\%}$; $u(\text{nCO}_2:\text{nIL}) = 0.01$; $u(\text{Temp}) = 0.5 \text{ }^\circ\text{C}$.

Table 2 Density, decomposition temperature and viscosity of the dry and wet superbase ILs used in this study.

| IL | ρ (g·cm ⁻³) at 25 °C | T_{dec} (°C) | η (mPa·s) at 25 °C | | | | | |
|--------------------------------|---|-------------------|----------------------------|---------------------------|--------------------------|----------------------------|---------------------------|--------------------------|
| | | | Dry | | | Wet | | |
| | | | Water content (wt %) | Before CO ₂ | After CO ₂ | Water content (wt %) | Before CO ₂ | After CO ₂ |
| [P ₆₆₆₁₄][124Triz] | 0.9019 | 304 | 0.046 | 569 | 638 | 11.27 | 114 | 200 |
| [P ₆₆₆₁₄][PhO] | 0.8955 | 252 | 0.033 | 240 | 368 | 6.51 ^a | 183 | 413 |
| [P ₆₆₆₁₄][Bentriz] | 0.9315 | 343 | 0.042 | 406 | 443 | 7.42 | 181 | 270 |
| [P ₆₆₆₁₄][123Triz] | 0.8993 | 281 | 0.078 | 434 | 419 | 11.57 | 106 | 129 |
| [P ₆₆₆₁₄][Benzim] | 0.9077 | 289 | 0.075 | 1149 | 388 | 8.62 | 207 | 230 |

^aCalculated from weight gain

$$u(\text{water content}) = (0.01 \times \text{water content}) \text{ wt}\%; u(\eta) = (0.01 \times \eta) \text{ mPa}\cdot\text{s}; u(\rho) = 10^{-4} \text{ g}\cdot\text{cm}^{-3}; \\ u(T_{dec}) = 1 \text{ }^{\circ}\text{C}; u(\text{Temp}) = 0.01 \text{ }^{\circ}\text{C}$$

Table 3 ^{13}C -NMR chemical shifts (ppm) for the additional peak observed after CO_2 absorption under dry and wet conditions.

| IL | Dry IL + CO_2 | Wet IL + CO_2 |
|--------------------------------|------------------------|------------------------|
| [P ₆₆₆₁₄][124Triz] | 160.62 | 160.17 |
| [P ₆₆₆₁₄][PhO] | 160.14 | 159.99 |
| [P ₆₆₆₁₄][Bentriz] | 160.16 | 160.34 |
| [P ₆₆₆₁₄][123Triz] | 160.44 | 160.28 |
| [P ₆₆₆₁₄][Benzim] | 160.45 | 160.23 |

CO₂ Capture in Wet and Dry Superbase Ionic Liquids

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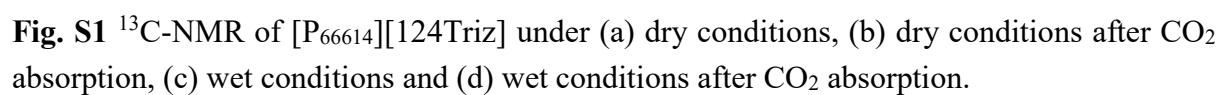
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Supporting Information

Table S1 CO₂ uptake over time under dry and wet conditions for all ILs studied at 22 °C and atmospheric pressure.

| IL | Test conditions | CO ₂ uptake (nCO ₂ :nIL) | | | | | | |
|--------------------------------|-----------------|--|--------|--------|--------|---------|---------|-----------------------|
| | | 5 min | 15 min | 30 min | 60 min | 120 min | 180 min | 960 min or stabilized |
| [P ₆₆₆₁₄][124Triz] | Dry | 0.60 | 0.80 | 0.85 | 0.92 | 0.99 | - | 1.01 |
| | Wet | 0.55 | 0.85 | 0.86 | 0.84 | 0.82 | 0.82 | 0.82 |
| [P ₆₆₆₁₄][PhO] | Dry | 0.33 | 0.40 | 0.44 | 0.49 | 0.64 | - | 1.00 |
| | Wet | 0.61 | 0.70 | 0.69 | 0.58 | 0.48 | 0.37 | 0.16 |
| [P ₆₆₆₁₄][Bentriz] | Dry | 0.08 | 0.13 | 0.17 | 0.23 | - | - | 0.39 |
| | Wet | 0.27 | 0.54 | 0.58 | 0.60 | 0.58 | 0.59 | 0.59 |
| [P ₆₆₆₁₄][123Triz] | Dry | 0.19 | 0.24 | 0.29 | 0.35 | 0.61 | - | 0.62 |
| | Wet | 0.40 | 0.68 | 0.77 | 0.76 | 0.68 | - | 0.65 |
| [P ₆₆₆₁₄][Benzim] | Dry | 0.82 | 1.00 | 1.03 | 1.06 | 1.20 | - | 1.20 |
| | Wet | 0.62 | 0.83 | 0.87 | 0.91 | 1.01 | 1.04 | 1.04 |

u(nCO₂:nIL) = 0.01; u(Temp) = 0.5 °C.



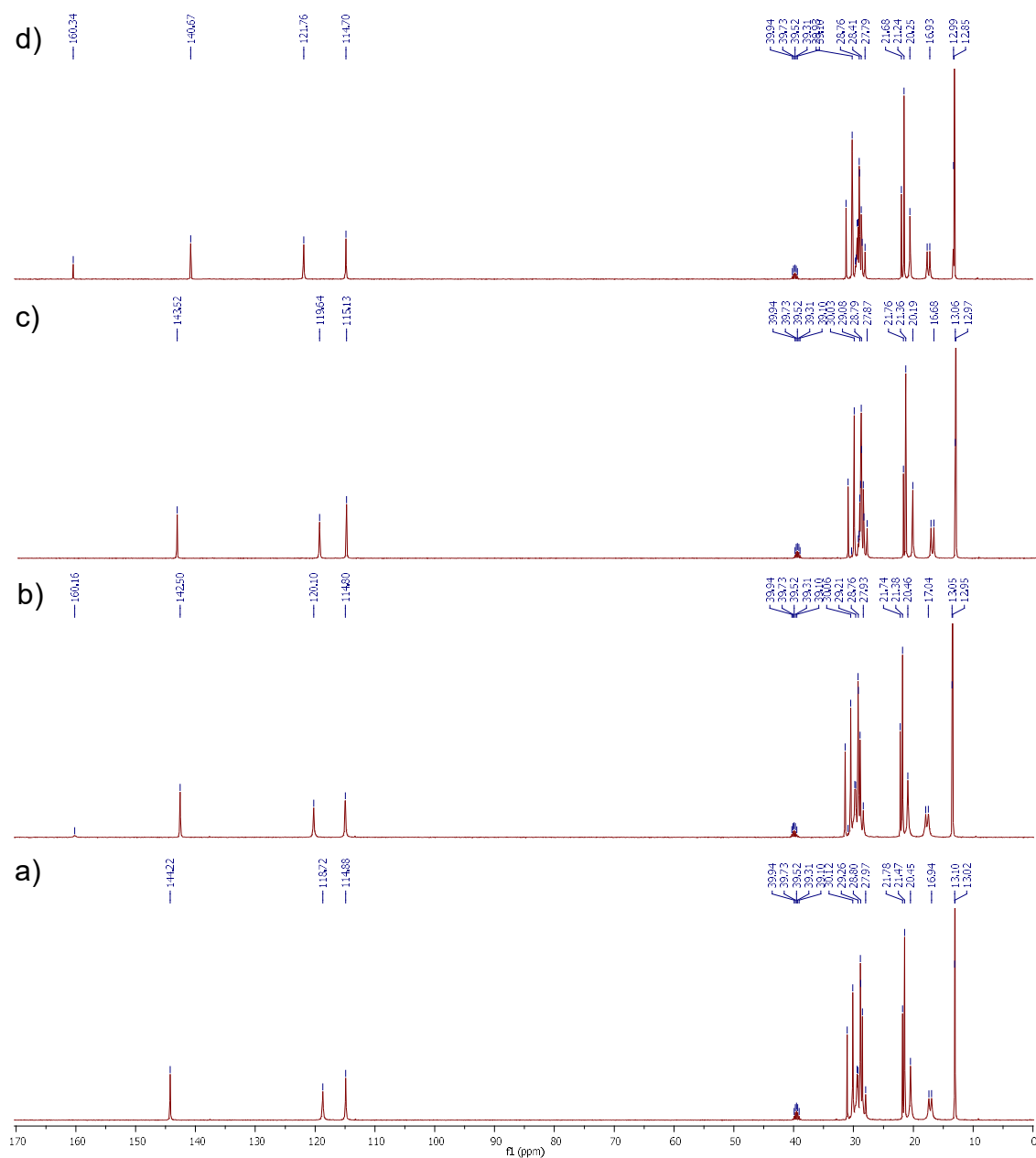


Fig. S2 ^{13}C -NMR of $[\text{P}_{66614}][\text{Bentriz}]$ under (a) dry conditions, (b) dry conditions after CO_2 absorption, (c) wet conditions and (d) wet conditions after CO_2 absorption.

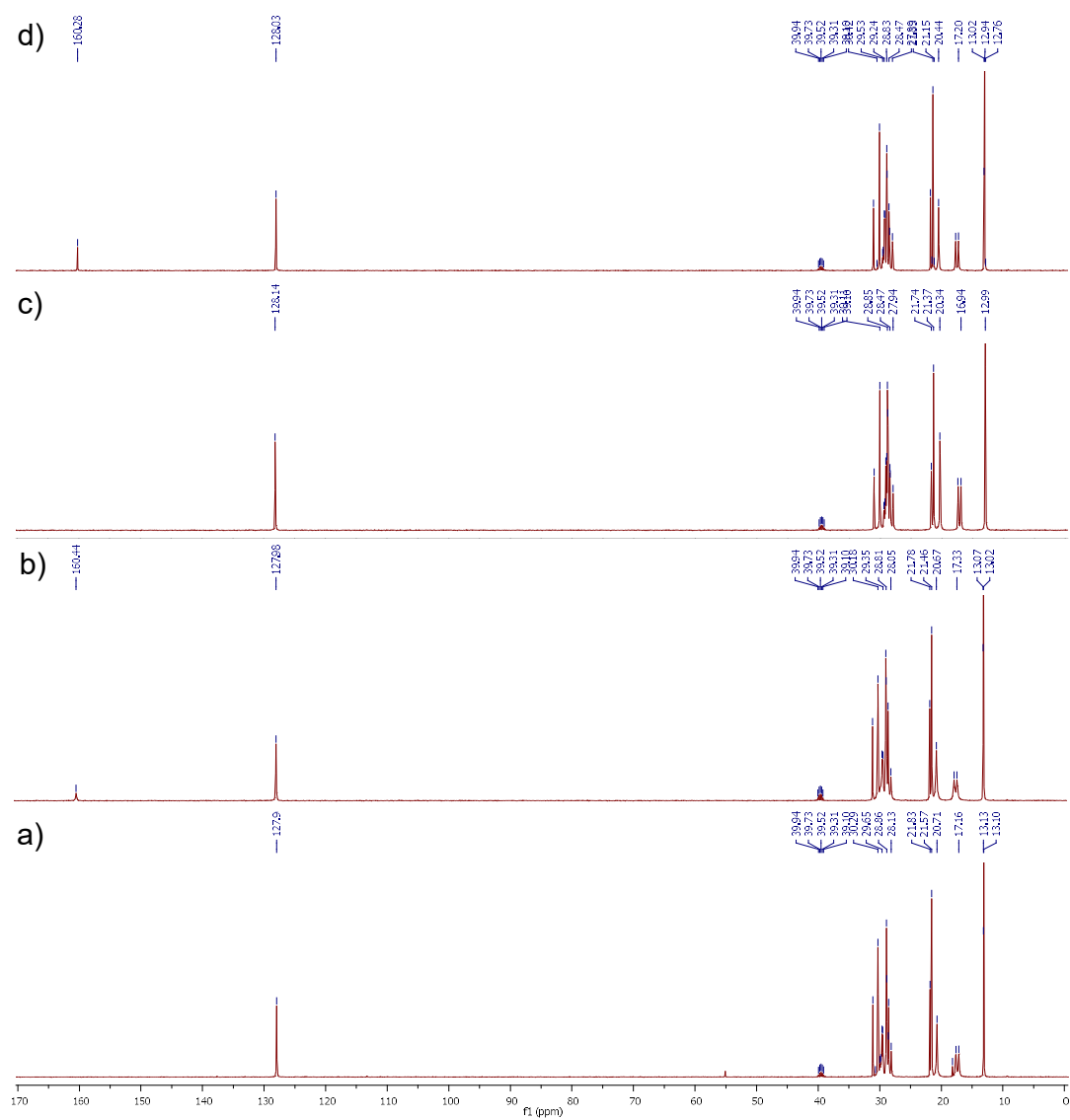


Fig. S3 ^{13}C -NMR of $[\text{P}_{66614}][123\text{Triz}]$ under (a) dry conditions, (b) dry conditions after CO_2 absorption, (c) wet conditions and (d) wet conditions after CO_2 absorption.

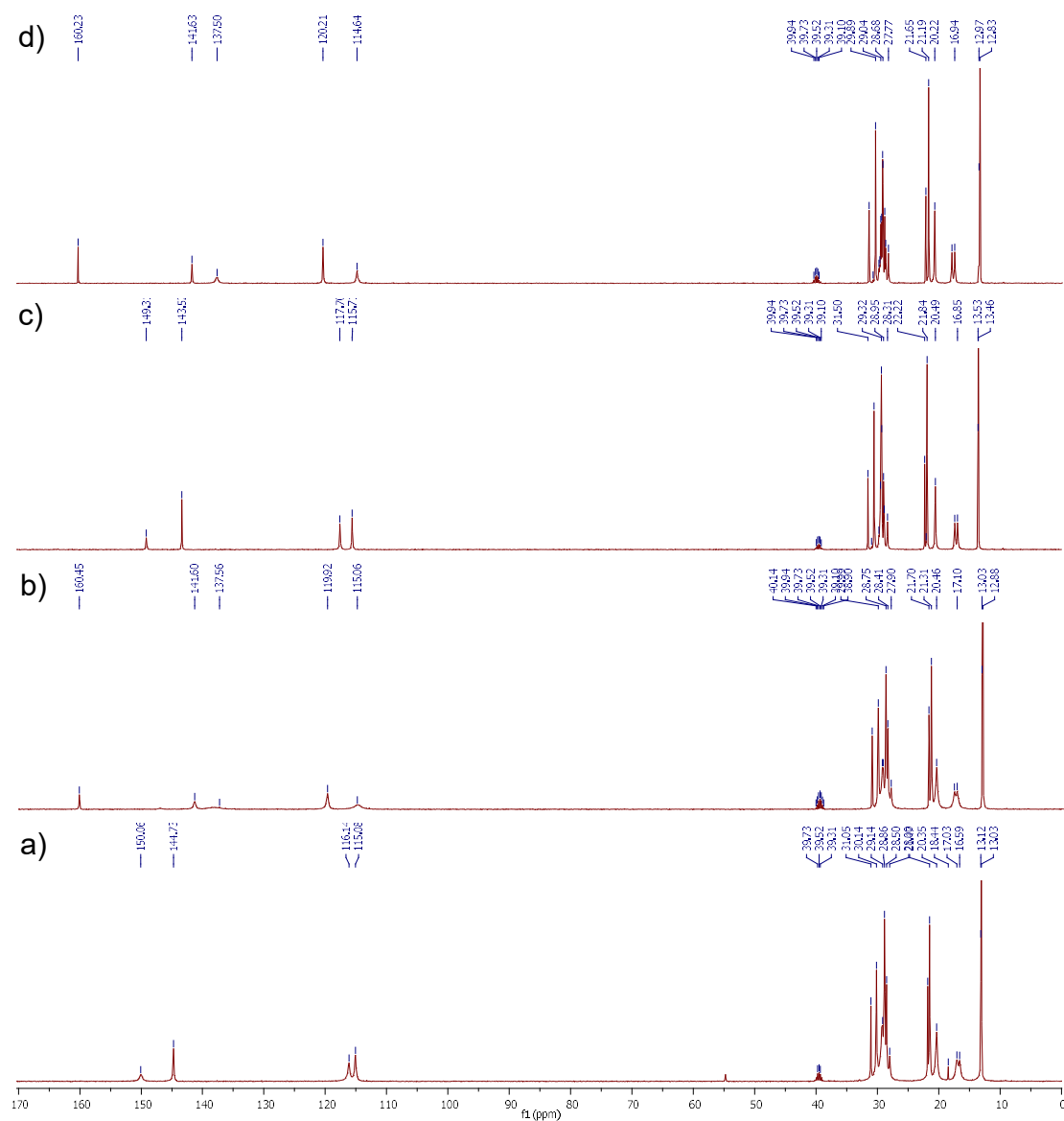


Fig. S4 ^{13}C NMR of $[\text{P}_{66614}][\text{Benzim}]$ under (a) dry conditions, (b) dry conditions after CO_2 absorption, (c) wet conditions and (d) wet conditions after CO_2 absorption.